

An Investigation of the Composition
of Certain Oxides of Manganese

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

—BY—

ARTHUR DOUGLAS CHAMBERS

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ACKNOWLEDGMENT.

This work was suggested by Professor H. N. Morse and was carried out under his direction. To him the author wishes to express his thanks. He also wishes to acknowledge his indebtedness to Professors Ira Remsen, W. B. Clarke, and the late Professor George H. Williams.

INTRODUCTORY.

The study of the composition of the oxides of manganese which lie between Mn_2O_3 and MnO , has attracted the attention of several chemists. A number of the comparatively simple compounds have been described from time to time, among these are $2\text{MnO}_3\text{MnO}_2$,¹ MnO_2MnO_2 ,² MnO_4MnO_2 ,³ MnO_5MnO_2 ,⁴ $\text{MnO}_{11}\text{MnO}_2$,⁵ $\text{MnO}_{23}\text{MnO}_2$.⁶ It is also well known that manganese dioxide prepared by wet methods has acid properties and forms insoluble salts with many bases, so that if manganese dioxide is precipitated from any solution in which salts are present, some of the base will be found in the precipitate.

During the session '93-'94 in this laboratory, the study of the composition of the oxides of manganese which are formed by the decomposition of the manganese dioxide, prepared by precipitating manganous sulphate by potassium permanganate, was undertaken by Morse and Walker. Their work had reference only to ratio of manganous oxide to available oxygen in the compounds. The results obtained are recorded in Walker's dissertation.

The work herein described is a continuation of that just mentioned. The composition of a number of oxides has been studied not only as regards the ratio of manganous oxide to available oxygen, but also with reference to the amount of water and base which they contain.

Special methods of analysis have been devised and some errors in older methods have been noted.

II. Preparation of Material.

Two different methods were used for the preparation of the manganese dioxide which formed the starting point in the

¹ Franke, J. prakt. Chem., **36**, 166.

² Reissig, Ann. Chem. (Liebig), **103**, 77.

³ Gorgen, Bull. Soc. Chim., **51**, 1.

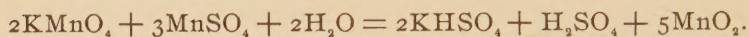
⁴ Gorgen, Bull. Soc. Chim., **51**, 1; Carnot, Bull. Soc. Chim. (3), **1**, 279.

⁵ Veley, J. Soc. Chim., **37**, 581.

⁶ Veley, J. Soc. Chim., **37**, 581.

work. In the first it was not attempted to get the oxide entirely free from other bases; in the second an attempt was made to prepare an oxide free from all bases except manganous oxide.

Method A.—Manganous sulphate was treated with an excess of potassium permanganate in the presence of nitric acid, the equation representing the reaction is the following :



The actual quantities used were 167 grams of crystallized manganous sulphate, 110 grams of potassium permanganate, and 252 grams of 70 per cent. nitric acid. The total volume of the mixed solutions amounted to about 3 liters, this made the nitric acid about normal strength in the solution, while there were about four molecules of nitric acid present for every atom of potassium. The precipitation was made at a temperature of about 65° C. by pouring the mixed nitric acid and manganous sulphate solutions into that of the permanganate, so that at all times there was an excess of the permanganate. The oxide was washed first by decantation, then filtered off on an asbestos filter and washed until free from impurities soluble in water. The ratio of manganous oxide to available oxygen was then determined and found to correspond to the formula MnO_2 .

This is essentially the method employed by Morse and Walker in the preparation of the oxides used by them.

Method B.—The essential difference between this and the method given above is that ammonium permanganate was used instead of the potassium salt. The ammonium permanganate was prepared as follows: Concentrated solutions of potassium permanganate and silver nitrate were mixed, the precipitated silver salt was filtered off, and twice recrystallized from water, the oxides which formed on heating being removed each time by filtering through asbestos. The silver salt was then ground in a large mortar with an equivalent amount of ammonium bromide, sufficient water being added to dissolve the ammonium permanganate. It cannot be prepared by mixing together hot solutions of the two salts on

account of the ready decomposition of the compound. When, however, the solution is freed from silver bromide and oxides of manganese by filtration, it can be heated to 65° C. with very little decomposition.

From this solution of ammonium permanganate the oxide was prepared as stated under *A*. It was washed with dilute nitric acid until a portion, when heated with strong caustic potash solution did not give enough ammonia to be detected by the odor or by litmus paper. It was found, however, when a quantitative analysis was made that it still contained about 0.2 per cent. of ammonia as well as a small amount of silver bromide.

III. Reagents used in Analysis.

1. *Potassium Permanganate Solution*.—Of this reagent two solutions were used, one of which contained about $3\frac{1}{2}$ grams per liter, the other about 8 grams per liter.

The weaker solution was used in titrating the excess of potassium tetroxalate in the analyses, and the stronger for the determination of manganese by the modified Volhard method. The solutions were made from permanganate purified by recrystallization from the commercial salt and were filtered twice through asbestos. Solutions made in this way can be kept for months with scarcely any decrease in strength.

2. *A Solution of Potassium Tetroxalate*.—This contained about fifteen grams of the salt per liter. A weaker solution is not satisfactory for this work on account of the length of time required to dissolve the oxides, especially after they have become very dry. On the other hand, if a very little stronger solution is used, the tetroxalate will crystallize out in cold weather.

3. *A Standard Solution of Sulphuric Acid*.—The strength of this was about 0.25 N. The concentration was determined gravimetrically by precipitation as barium sulphate, also by a standard permanganate solution according to the method recently described.¹ The results obtained by the two methods showed very close agreement.

¹ Morse and Chambers, *Am. Chem. J.*, 18, 236.

4. *A Solution of Ammonia.*—This was approximately $\frac{1}{10}$ N. strength. It was made from a solution which had been freed from carbonate by distilling it from lime. Its relation to the sulphuric acid was determined from time to time.

5. *Zinc Oxide which contained no Reducing Substances.*—This was prepared by igniting the commercial oxide for three or four hours in a muffle. This, when dissolved in sulphuric acid, gave a solution which did not reduce permanganate.

6. *A Neutral Solution of Zinc Sulphate of Definite Strength which did not Reduce Permanganate.*—This was easily prepared by heating a known amount of sulphuric acid with an excess of zinc oxide, prepared as described above, until the solution was neutral. It was then diluted to a definite volume. The concentration of the solution used was 200 grams per liter.

7. *A Neutral Solution of Hydrogen Peroxide.*—This was prepared by shaking the ordinary solution for some time with zinc oxide. The excess of the oxide was removed by filtering through asbestos.

8. *Water which was Neutral to Litmus and Contained no Reducing Substances.*—This was prepared from the ordinary distilled water in the following manner: A six-liter flask was connected with a retort, of about $2\frac{1}{2}$ liters capacity, by a large glass tube, which passed through the tubulure and to the bottom of the retort. The retort neck was directed upwards at an angle of about 45° and was joined by means of an adapter to a Liebig's condenser. All the openings in the apparatus, except the neck of the flask were closed with asbestos and asbestos paper, as it was found that cork and rubber stoppers were decomposed by the steam and that substances passed over with the water which reduced permanganate. The flask contained distilled water acidified with sulphuric acid, and the retort a strong alkaline solution of potassium permanganate. Both solutions were heated to boiling, and the heat was then so regulated that the volume of the solution in the retort remained nearly constant while the steam passed from the flask through it. A large plug of glass wool in the

adapter prevented any carrying over of oxides of manganese. Water purified in this way was used in the preparation of reagents and in all the analyses.

IV. Methods of Analysis.

The measuring flasks used were graduated by the methods of Morse and Blalock.¹ The burettes were also calibrated by their method, so that in the titrations volumes could be accurately measured to the $\frac{1}{100}$ of a cc.

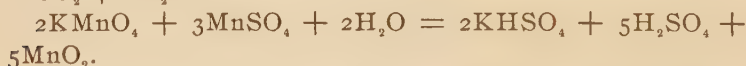
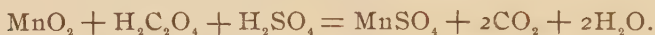
A. To Determine the Ratio of Manganous Oxide to Available Oxygen.

For this there were required the tetroxalate and permanganate solutions. It is not necessary to know their absolute strength but only the relation between them. About 0.2 gram of an oxide was placed in a beaker of about 150 cc. capacity and an excess of the tetroxalate measured in, then 5-10 cc. of a 25 per cent. solution of sulphuric acid were added. The beaker was placed in an air-bath heated to 60° C. and stirred occasionally until all the oxide had dissolved. The excess of the tetroxalate was then determined by the weaker permanganate solution. The solution was then poured into a liter florence flask and zinc oxide added until the sulphuric acid was neutralized and a small amount of the oxide remained in suspension. A small excess is an advantage since it neutralizes the sulphuric acid formed in the subsequent reaction, but a considerable excess is to be avoided, because it obscures the end reaction. Five grams of zinc sulphate were then added and the solution heated to boiling. Into another flask of the same size there was then drawn off from a burette the amount of permanganate necessary to precipitate the manganese, assuming the oxide to be manganese dioxide, as well as enough to precipitate the manganese derived from the permanganate used in titrating the excess of tetroxalate. The boiling solution of manganese sulphate was then rapidly poured into this and the flask rinsed three or four times with hot water. The flask was

¹ Am. Chem. J., 16, 479.

then shaken five or six times and the precipitate allowed to settle. More permanganate was then added from the burette until the solution retained the pink color after shaking ten or twelve times. Since the difficulty in this method is altogether in the determination of manganese, it was found advantageous in the latter part of the work to make up the manganous sulphate solution to 200 cc. and to determine the manganese in 50 cc. portions of this, each time drawing off to within $\frac{1}{10}$ cc., the amount of permanganate required in the preceding analysis. The first result is generally a little low, the subsequent ones show close agreement. Of course, about four times as much oxide must be reduced when this method is used.

The equations representing the reactions involved in the above method are the following:



Oxalic acid is written instead of potassium tetroxalate, as it simplifies the equations.

Now one molecule of manganese dioxide contains $\frac{2}{5}$ as much available oxygen as one molecule of potassium permanganate.

One molecule of manganous sulphate requires $\frac{2}{3}$ of one molecule of potassium permanganate to precipitate it.

Now in an analysis the ratio of the number of molecules of permanganate which are equivalent in available oxygen to the number of molecules of manganese dioxide present, to the number of molecules of permanganate required to precipitate the manganese derived from the manganese dioxide is $\frac{2}{5} : \frac{2}{3}$, or 6 : 10; or the number of cc. of permanganate which are equivalent to the number of cc. of tetroxalate oxidized by the manganese dioxide multiplied by $\frac{1}{6}$ is equal to the number of cc. of permanganate required to precipitate the manganese. Now if more than this amount is used, the oxide contains relatively more manganese than available oxygen, and

the ratio of the number of cc. used to the number calculated as above is the ratio of the total number of molecules of manganous oxide to the number of molecules of manganese dioxide, or, since each molecule of manganese dioxide contains one atom of available oxygen, of manganous oxide to oxygen.

Of course, in an actual determination the number of cc. of permanganate used to precipitate the manganous sulphate must be corrected for the manganese introduced in titrating the excess of tetroxalate. This is done by deducting $\frac{2}{3}$ of the number of cc. introduced, since one molecule of potassium permanganate gives one molecule of manganous sulphate, which requires $\frac{2}{3}$ of one molecule of potassium permanganate to precipitate it.

Remarks on the Method.

It will be seen from the previous statements that the Volhard method for the determination of manganese has been considerably modified. In the Volhard method, as ordinarily employed, the potassium permanganate solution is run from a burette into the hot manganous sulphate solution, which contains zinc sulphate and one or two drops of nitric acid. The accuracy of this method was tested as follows: A certain number of cc. of permanganate solution were exactly reduced by the tetroxalate. It should require $\frac{2}{3}$ of the number of cc. reduced to precipitate the manganese as manganese dioxide. It was found, however, that the end reaction was obtained before this amount had been added except when very small quantities were used.

A few of the results obtained are given below.

Column I contains the calculated number of cc. required to precipitate the manganese, *i. e.*, $\frac{2}{3}$ of the number of cc. reduced.

Column II the number of cc. required.

Column III the amount of manganese in the solution.

Column IV the amount of manganese found.

Column V the deficiency in per cent.

I.	II.	III.	IV.	V.
20.09	20.04	0.1035	0.1032	0.29
30.15	30.07	0.15525	0.15497	0.24
41.63	41.38	0.21441	0.21312	0.60
53.30	52.84	0.26451	0.27214	0.86

The error increases rapidly as the amount of manganese increases. By using the modified method, however, accurate results could be obtained as long as the manganese in the solution did not exceed 0.15 gram. When larger quantities were used, low results were always obtained, and the error increased with increasing quantities of manganese, just as in the other method, although it was very much smaller. The probable reasons for the greater accuracy are the following :

1. In mixing the manganous sulphate and the permanganate solutions, there is an excess of permanganate almost to the end of the reaction, thus decreasing the chances of formation of any oxides of manganese lower in oxygen than manganese dioxide.

2. The solution is kept very nearly neutral to the end of the determination, the excess of zinc oxide neutralizing the sulphuric acid as soon as formed.

3. The necessity of using nitric acid is obviated by using purified water.

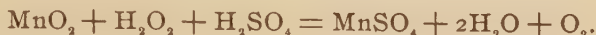
It has been shown that manganese dioxide will decompose potassium permanganate quite readily in the presence of either sulphuric or nitric acid at a temperature near 100° C.

B. Methods Used for the Determination of the Percentage Composition of Oxides Containing Manganous Oxide, Potassium Oxide or Ammonia, Water and Oxygen.

1. *Manganous Oxide.*—This was determined by reducing about 0.2 gram of the oxide with sodium sulphite and sulphuric acid, evaporation of the excess of sulphur dioxide and precipitation of the manganese by the modified Volhard method. This gave the per cent. of manganous oxide.

2. *Total Base.*—This consisted of manganous oxide and either potassium oxide or ammonia. About 0.2 gram was

treated with an excess of standard sulphuric acid and hydrogen peroxide and warmed until the oxide had completely dissolved. The excess of the acid was then determined by titration with a solution of ammonia, using litmus as the indicator. The reaction involved in the solution of the oxide is expressed by the equation :



A large excess of hydrogen peroxide should be avoided, because it impairs the sensibility of the indicator, also because it produces a precipitate of oxide in the solution as each drop of ammonia is added. This dissolves readily by stirring as long as the solution is acid. The precipitation can, however, be almost entirely avoided by using only a slight excess of the peroxide. This method gave the amount of sulphuric acid neutralized by the manganous oxide and potassium oxide or ammonia, that required for the manganous oxide is easily calculated from the previous determination by the Volhard method, the difference is that neutralized by the potassium oxide or ammonia from which their per cent. can be easily calculated.

3. *Ammonia*.—In addition to the above method the ammonia was determined by reducing a portion with sulphurous acid and sulphuric acid, transferring to a Kjeldahl distilling apparatus, rendering alkaline with potassium hydroxide and absorption of the ammonia in standard sulphuric acid. The results by the two methods showed close agreement. The silver bromide present as an impurity in a number of samples was determined in the same portion by filtering it off and weighing after the oxide had dissolved.

4. *Available Oxygen*.—This was determined in a weighed portion in the same manner as directed under *A.*, except that the tetroxalate solution was carefully standardized. From the number of cc. required to dissolve the oxide the per cent. of available oxygen was calculated.

The manganous oxide, potassium oxide or ammonia and available oxygen can all be determined in the same portion, if

desired, as follows: Dissolve in a solution of potassium tetroxalate and standard sulphuric acid, titrate the excess of tetroxalate with permanganate, then add one or two drops of hydrogen peroxide to prevent precipitation of oxide, and titrate the excess of acid by ammonia, then acidify again and destroy the hydrogen peroxide with permanganate and determine the total manganese by the Volhard method.

Owing to the complexity of this method and the corrections to be introduced at each step, it was seldom used.

5. *To Determine the Ratio of Potassium Oxide to Manganous Oxide in the Same Sample.*—Dissolve standard sulphuric acid with addition of hydrogen peroxide, titrate the excess of acid with ammonia, then acidify and titrate the excess of hydrogen peroxide with permanganate, then determine the total manganese by the Volhard method. Knowing the relation existing between the sulphuric acid and permanganate, the ratio of potassium oxide to manganous oxide is readily calculated.

6. *Determination of Water. (a) When the Oxide Contained Ammonia.*—About 0.5 gram was weighed into a platinum boat and placed in a combustion tube in a short gas furnace, two weighed glass-stoppered U-tubes containing glass beads and sulphuric acid were attached to each end of the tube. A slow current of air, dried by sulphuric acid, was passed through the apparatus. The U-tubes contained just enough sulphuric acid so that the air was forced to pass through it. The oxide was then heated and the water collected in the tubes.

It was found that the result must be corrected for the amount of water formed from the ammonia. No free ammonia is given off. This was proved by attaching a Peligot tube containing standard acid to the apparatus and heating some oxide as before. It was found that no acid was neutralized.

(7) *When the Oxide Contained Potassium Oxide.*—The method of procedure was exactly the same in this case as in the preceding, except that the oxide was mixed with lead monoxide to facilitate the elimination of water. In some cases chromium oxide (Cr_2O_3) was used.

V. Accuracy of these Methods.

It is not considered possible by these methods to distinguish between two such compounds as $\text{MnO}_{19}\text{MnO}_3$ and $\text{MnO}_{20}\text{MnO}_3$. It is believed, however, $\text{MnO}_{19}\text{MnO}_3$ can be distinguished from $\text{MnO}_{21}\text{MnO}_3$, but this is the limit of their accuracy. The percentage composition of the three compounds is given below :

	MnO.	O ₂ .
$\text{MnO}_{19}\text{MnO}_3$	82.35	17.65
$\text{MnO}_{20}\text{MnO}_3$	82.32	17.68
$\text{MnO}_{21}\text{MnO}_3$	82.28	17.72

VI. The Results of Analyses.

Oxide No. 1.—This was prepared June 10, '95, by method B. It was placed in a glass dish in a desiccator containing sulphuric acid. It was exposed only to diffused light. Analyzed March 2, '96:

	Found.	Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{20}\text{MnO}_3 + 6\text{H}_2\text{O}$.
MnO	77.27	77.77	77.68
O ₂	16.65	16.76	16.69
H ₂ O	5.21	5.24	5.63
NH ₃	0.14		
AgBr	0.50		
	99.77	99.77	100.00

Oxide No. 2.—Prepared June 10, '95. It was placed in a crystallizing dish in a desiccator containing sulphuric acid. It was exposed to the direct rays of the sun. Analyzed Feb. 25, '96.

	Found.	Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{20}\text{MnO}_3 + 6\text{H}_2\text{O}$.
MnO	77.37	77.70	77.68
O ₂	16.82	16.90	16.69
H ₂ O	5.38	5.40	5.63
NH ₃ + AgBr	0.43		
	100.00	100.00	100.00

This oxide was lost by an accident after the first three determinations were made. The calculations were made by determining the ammonia and silver bromide by difference.

Oxide No. 3.—This was prepared June 10, '95, by method *B*. It was placed in a glass dish in a desiccator containing phosphorus pentoxide. It was exposed only to diffused light. It was analyzed March 5, '96.

	Found.	Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{20}\text{MnO}_2 + 6\text{H}_2\text{O}$.
MnO	77.13	77.91	77.68
O_2	16.43	16.59	16.69
H_2O	5.55	5.62	5.63
NH_3	0.22		
AgBr	0.79		
	100.12	100.12	100.00

Oxide No. 4.—Prepared June 10, '95, by method *B*. It was placed in a small dish in a desiccator containing phosphorus pentoxide. It was exposed to the direct sunlight. Analyzed March 11, '96.

	Found.	Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{20}\text{MnO}_2 + 4\text{H}_2\text{O}$.
MnO	78.70	79.37	79.17
O_2	16.85	16.99	17.01
H_2O	3.58	3.61	3.83
NH_3	0.14		
AgBr	0.71		
	99.98	99.97	100.00

This oxide had apparently lost two molecules more water than the preceding one. This was probably due to the fact that the latter was subjected to a much higher temperature during the summer months, as it stood in the sunlight.

Oxide No. 5.—This oxide was prepared June 10, '95, by method *B*. It was placed in a glass dish in a desiccator which contained calcium chloride. It was exposed only to diffused light. Analyzed March 16, '96.

	Found.	Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{12.5}\text{MnO}_2 + 5\text{H}_2\text{O}$.
MnO	75.96	76.64	76.75
O_2	15.79	15.93	16.03
H_2O	7.37	7.44	7.22
NH_3	0.21		
AgBr	0.68		
	100.01	100.01	100.00

Oxide No. 6.—This was prepared June 10, '95, by method *B*. It stood in the sunlight in a desiccator containing calcium chloride. It was analyzed March 19, '96.

	Found.	Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{12.5}\text{MnO}_3 + 5.5\text{H}_2\text{O}$
MnO	75.63	76.29	76.21
O_2	15.77	15.91	15.91
H_2O	7.49	7.55	7.88
NH_3	0.20		
AgBr	0.66		
	99.75	96.75	100.00

This oxide and the preceding one, both standing over calcium chloride, contained much less oxygen than those which stood over the more effective drying agents. A possible explanation of this is that it was due to the alternate absorption and loss of water by the oxides as the calcium chloride has a large temperature coefficient.

Oxide No. 7.—This was prepared June 10, '95, by method *B*. It was placed in a glass crystallizing dish in a desiccator which contained about 250 cc. of water. Although it stood in an atmosphere saturated with water vapor, it was quite dry and readily powdered. This was no doubt due to the fact that it stood in the sunlight and was at times heated to a considerable extent. It was analyzed March 24, '96.

	Found.	Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{15}\text{MnO}_3 + 4.5\text{H}_2\text{O}$.
MnO	77.34	78.06	77.95
O_2	16.34	16.49	16.48
H_2O	5.52	5.57	5.56
NH_3	0.22		
AgBr	0.70		
	100.12	100.12	100.00

Oxide No. 8.—This oxide was prepared June 10, '95, by method *B*. It was placed in a beaker, covered with about 150 cc. of water and enclosed in a desiccator. It was exposed to the sunlight. Owing to an imperfectly fitting cover the water escaped during the summer months. It was analyzed April 8, '96, and gave the following results :

		Corrected for $\text{NH}_3 + \text{AgBr}$.	Calculated for $\text{MnO}_{20}\text{MnO}_9 + 3.5\text{H}_2\text{O}$.
MnO	78.83	79.59	79.55
O ₂	16.85	17.01	17.09
H ₂ O	3.24	3.27	3.36
NH ₃	0.27		
AgBr	0.69		
	99.88	99.87	100.00

Oxide No. 9.—This oxide was prepared June 10, '95, by method *B*. It was placed in a crystallizing dish in a desiccator which contained about 200 cc. of water. Unlike the oxide which was placed in the sunlight, this oxide lost scarcely any water, and was still of the consistency of a thick paste. Since a complete analysis of it in this condition could not be satisfactorily made, only the ratio of manganous oxide to oxygen was determined. It was analyzed March 26, '96.

Ratio MnO : O found	I : 0.9482
Calculated for $\text{MnO}_{18}\text{MnO}_9$	I : 0.9474

Oxide No. 10.—Prepared June 10, '95, by method *B*. It was placed in a beaker, covered with about 150 cc. of water and enclosed in a desiccator. It was exposed only to diffused light. It was analyzed April 10, '96.

Ratio of MnO : O found	I : 0.9523
Calculated for $\text{MnO}_{20}\text{MnO}_9$	I : 0.9524

This completes the series of oxides prepared by method *B*. Those following all contained potassium oxide. Complete analyses were made of some, while in other cases only the ratio of manganous oxide to oxygen was determined.

Oxide No. 11.—This was prepared Oct. 20, '94, according to method *A*. It was placed in a desiccator containing phosphorus pentoxide and allowed to stand in a position exposed only to diffused light. Its composition as regards the ratio of manganous oxide to oxygen at different times was as follows :

Jan. 4, '95,	Ratio MnO : O found	1 : 0.9854
	Calculated for $\text{MnO}_{70}\text{MnO}_2$	1 : 0.9859
Mar. 27, '95,	Ratio MnO : O found	1 : 0.9658
	Calculated for $\text{MnO}_{28}\text{MnO}_2$	1 : 0.9655
May 8, '95,	Ratio MnO : O found	1 : 0.9646
	Calculated for $\text{MnO}_{27}\text{MnO}_2$	1 : 0.9643
April 15, '96,	Ratio MnO : O found	1 : 0.9654
	Calculated for $\text{MnO}_{28}\text{MnO}_2$	1 : 0.9655

It will thus be seen that the composition remained practically constant from March 27, '95, to April 15, '96. A complete analysis was made on the latter date with the following results :

	Found.	Calculated for $3\text{MnO}_{82}\text{MnO}_{238}\text{H}_2\text{O}_{.4}\text{K}_2\text{O}$.
MnO	71.60	71.76
O ₂	15.59	15.61
H ₂ O	8.14	8.14
K ₂ O	4.58	4.49
	99.91	100.00

Oxide No. 12.—This was prepared by method *A* on Oct. 20, '94. It was placed in a desiccator containing phosphorus pentoxide and exposed to the sunlight. Its composition was as follows :

Jan. 8, '95,	Ratio MnO : O	1 : 0.9720
	Calculated for $\text{MnO}_{35}\text{MnO}_2$	1 : 0.9722
Mar. 22, '95,	Ratio MnO : O	1 : 0.9520
	Calculated for $\text{MnO}_{20}\text{MnO}_2$	1 : 0.9524
May 18, '95,	Ratio MnO : O	1 : 0.9522
	Calculated for $\text{MnO}_{20}\text{MnO}_2$	1 : 0.9524
April 20, '96,	Ratio MnO : O	1 : 0.9428
	Calculated for $\text{MnO}_{16.5}\text{MnO}_2$	1 : 0.9428

This oxide slowly lost oxygen until it reached the composition $\text{MnO}_{20}\text{MnO}_2$, where it remained for some time. During the following year, however, it lost still more and finally attained the composition given above. A complete analysis was made April 20, '96.

	Found.	Calculated for $5\text{MnO}_{75}\text{MnO}_{44}\text{H}_2\text{O}_4\text{K}_2\text{O}$.
MnO	70.35	70.54
O_2	14.96	14.92
H_2O	9.86	9.85
K_2O	4.70	4.69
	99.87	100.00

Oxide No. 13.—Prepared Oct. 20, '94, by method *A*. It was placed in a desiccator containing calcium chloride in a position exposed to the direct sunlight. The analyses were as follows :

Jan. 9, '95,	Ratio MnO : O	1 : 0.9681
	Calculated for $\text{MnO}_{30}\text{MnO}_2$	1 : 0.9677
Mar. 22, '95,	Ratio MnO : O	1 : 0.9521
	Calculated for $\text{MnO}_{20}\text{MnO}_2$	1 : 0.9524
May 16, '95,	Ratio MnO : O	1 : 0.9436
	Calculated for $\text{MnO}_{16.5}\text{MnO}_2$	1 : 0.9428
April 23, '96,	Ratio MnO : O	1 : 0.9229
	Calculated for $\text{MnO}_{12}\text{MnO}_2$	1 : 0.9230

A complete analysis made April 23, '96, gave the following results :

	Found.	Calculated for $5\text{MnO}_{58}\text{MnO}_{40}\text{H}_2\text{O}_3\text{K}_2\text{O}$.
MnO	69.90	69.83
O_2	14.55	14.50
H_2O	11.31	11.25
K_2O	4.13	4.42
	99.89	100.00

Oxide 14.—Prepared Oct. 20, '94, by method *A*. It was placed in a beaker covered with about 150 cc. of water and enclosed in a desiccator. It was exposed to the sunlight. Its composition was as follows :

Jan. 10, '95.	Ratio MnO : O	1 : 0.9878
	Calculated for $\text{MnO}_{80}\text{MnO}_2$	1 : 0.9876

When the next analysis came to be made it was found that the water had escaped so that for all the subsequent analyses a dry oxide was used.

Mar. 26, '95,	Ratio MnO : O	1 : 0.9656
	Calculated for $\text{MnO}_{28}\text{MnO}_3$	1 : 0.9655
May 20, '95,	Ratio MnO : O	1 : 0.9635
	Calculated for $\text{MnO}_{26}\text{MnO}_3$	1 : 0.9630
May 5, '96.	Ratio MnO : O	1 : 0.9585
	Calculated for $\text{MnO}_{23}\text{MnO}_3$	1 : 0.9583

A complete analysis made May 5, '96, gave the following results :

	Found.	Calculated for $2\text{MnO}_{41}\text{MnO}_{22}\text{K}_2\text{O}_{11}\text{H}_2\text{O}$.
MnO	73.92	74.21
O_2	15.98	15.92
H_2O	4.97	5.06
K_2O	4.82	4.81
	99.69	100.00

Oxide No. 15.—This was prepared Oct. 20, 1894, by method *A*. It was placed in a crystallizing dish in a desiccator, which contained about 250 cc. of water. The oxide remained moist for some time, but, when the complete analysis was made it was quite dry and easily powdered, although it stood in an atmosphere saturated with water vapor. The results of the analysis were as follows :

Jan. 9, '95.	Ratio MnO : O	1 : 0.9840
	Calculated for $\text{MnO}_{60}\text{MnO}_3$	1 : 0.9836
Mar. 25, '95.	Ratio MnO : O	1 : 0.9596
	Calculated for $\text{MnO}_{24}\text{MnO}_3$	1 : 0.9600
May 18, '95.	Ratio MnO : O	1 : 0.9562
	Calculated for $\text{MnO}_{22}\text{MnO}_3$	1 : 0.9565
May 18, '96.	Ratio MnO : O	1 : 0.9513
	Calculated for $\text{MnO}_{20}\text{MnO}_3$	1 : 0.9524

The complete analysis, made May 18, '96, gave the following results :

	Found.	Calculated for $5\text{MnO}_{94}\text{MnO}_{25}\text{K}_2\text{O}_{55}\text{H}_2\text{O}$.
MnO	70.05	70.31
O_2	15.03	15.06
K_2O	4.77	4.72
H_2O	9.94	9.91
	99.79	100.00

Oxide No. 16.—This was prepared Oct. 20, '94, by method *A*. It stood in a desiccator over sulphuric acid in diffused light. The analyses were as follows :

Jan. 3, '95,	Ratio MnO : O	1 : 0.9822
	Calculated for $\text{MnO}_{55}\text{MnO}_2$	1 : 0.9821
April 1, '95,	Ratio MnO : O	1 : 0.9613
	Calculated for $\text{MnO}_{25}\text{MnO}_2$	1 : 0.9615
May 11, '95,	Ratio MnO : O	1 : 0.9614
	Calculated for $\text{MnO}_{25}\text{MnO}_2$	1 : 0.9615

Oxide No. 17.—Prepared Oct. 20, '94, by method *A*. This oxide was placed in a desiccator over calcium chloride and was exposed to diffused light only. The results of analyses were as follows :

Jan. 5, '95.	Ratio MnO : O	1 : 0.9835
	Calculated for $\text{MnO}_{60}\text{MnO}_2$	1 : 0.9836
Mar. 29, '95.	Ratio MnO : O	1 : 0.9522
	Calculated for $\text{MnO}_{20}\text{MnO}_2$	1 : 0.9524
May 13, '95.	Ratio MnO : O	1 : 0.9526
	Calculated for $\text{MnO}_{20}\text{MnO}_2$	1 : 0.9524

Oxide No. 18. This was prepared Oct. 23, '94, by method *A*. It was spread out on a drying plate and kept under a bell jar. The analyses were as follows :

Jan. 7, '95.	Ratio MnO : O	1 : 0.9904
	Calculated for $\text{MnO}_{100}\text{MnO}_2$	1 : 0.9901
April 8, '95.	Ratio MnO : O	1 : 0.9719
	Calculated for $\text{MnO}_{35}\text{MnO}_2$	1 : 0.9722
May 23, '95.	Ratio MnO : O	1 : 0.9689
	Calculated for $\text{MnO}_{31}\text{MnO}_2$	1 : 0.9687

Oxide No. 19.—This was prepared Oct. 20, '94, by method *A*. It was placed in a beaker, covered with about 150 cc. of water, and enclosed in a desiccator. It stood in diffused light. The analyses were as follows :

Jan. 7, '95.	Ratio MnO : O	1 : 0.9905
	Calculated for $\text{MnO}_{100}\text{MnO}_2$	1 : 0.9901

April 3, '95.	Ratio MnO : O	1 : 0.9760
	Calculated for $\text{MnO}_{40}\text{MnO}_2$	1 : 0.9756
May 14, '95.	Ratio MnO : O	1 : 0.9690
	Calculated for $\text{MnO}_{31}\text{MnO}_2$	1 : 0.9687
May 8, '96.	Ratio MnO : O	1 : 0.9673
	Calculated for $\text{MnO}_{30}\text{MnO}_2$	1 : 0.9677

Oxide No. 20.—This was prepared Oct. 20, '94, by method A. It stood in a desiccator over water in diffused light.

The analyses were as follows :

Jan. 7, '95.	Ratio MnO : O	1 : 0.9648
	Calculated for $\text{MnO}_{200}\text{MnO}_2$	1 : 0.9950
April 2, '95.	Ratio MnO : O	1 : 0.9679
	Calculated for $\text{MnO}_{30}\text{MnO}_2$	1 : 0.9677
May 15, '95.	Ratio MnO : O	1 : 0.9670
	Calculated for $\text{MnO}_{29}\text{MnO}_2$	1 : 0.9667
May 9, '96.	Ratio MnO : O	1 : 0.9460
	Calculated for $\text{MnO}_{17.5}\text{MnO}_2$	1 : 0.9459

Oxide No. 21.—This was prepared Oct. 23, '94, by method A. It stood from that time until January 10, '95, under a bell-jar, when it was placed on a watch glass in a desiccator which contained a strong alkaline solution of pyrogallol. It was analyzed Jan. 7, 1895, and the ratio of manganous oxide to oxygen corresponded to the formula $\text{MnO}_{100}\text{MnO}_2$. The subsequent analyses were as follows :

Mar. 28, '95.	Ratio MnO : O	1 : 0.9655
	Calculated for $\text{MnO}_{28}\text{MnO}_2$	1 : 0.9655
May 12, '95.	Ratio MnO : O	1 : 0.9643
	Calculated for $\text{MnO}_{27}\text{MnO}_2$	1 : 0.9643
Jan. 24, '96.	Ratio MnO : O	1 : 0.9559
	Calculated for $\text{MnO}_{22}\text{MnO}_2$	1 : 0.9565

Oxide No. 22.—This was prepared Oct. 23, '94, by method A. It stood from that time until Jan. 20, '95, on a drying plate. At that time it was placed in a beaker and about 100 cc. of 2 N. nitric acid poured over it. It was then placed under a bell-jar, and was exposed to diffused light only. The ratio of the manganous oxide to oxygen was determined

a few days before it was placed under the nitric acid, and found to correspond to the formula $\text{MnO}_{100}\text{MnO}_2$. The ratio of the manganous oxide to oxygen and of the potassium oxide to manganous oxide was determined May 12, '96. The results were as follows :

Ratio of $\text{MnO} : \text{O}$	1 : 0.9622
Calculated for $\text{MnO}_{25}\text{MnO}_2$	1 : 0.9615
Ratio of $\text{K}_2\text{O} : \text{MnO}$	1 : 046.00

The solution over the oxide was found to contain considerable manganese.

Oxide No. 23.—This was another portion of the same oxide as No. 22. It was placed under 3 N. nitric acid at the same time. The results of analyses were as follows :

May 12, '96. Ratio $\text{MnO} : \text{O}$	1 : 0.9527
Calculated for $\text{MnO}_{20}\text{MnO}_2$	1 : 0.9524
Ratio of $\text{K}_2\text{O} : \text{MnO}$	1 : 40.00

There was also found to be considerable manganese in solution.

Oxide No. 24.—This was a third portion of the same oxide which was placed under 4 N. nitric acid. The other conditions were the same. The analyses were as follows :

May 13, '96. Ratio $\text{MnO} : \text{O}$	1 : 0.9591
Calculated for $\text{MnO}_{24}\text{MnO}_2$	1 : 0.9600
Ratio of $\text{K}_2\text{O} : \text{MnO}$	1 : 46.00

Conclusions.

1. There is a considerable error in the Volhard method for the determination of manganese, which can largely be avoided by a slightly different method of procedure.

2. In the decomposition of manganese dioxide, prepared by wet methods, there is a strong tendency to form compounds of the general formula, $\text{MnO } 2.5x\text{MnO}_2$, especially those which lie between $\text{MnO}_{10}\text{MnO}_2$ and $\text{MnO}_{30}\text{MnO}_2$. The compound $\text{MnO}_{20}\text{MnO}_2$ seems to be formed most frequently.

Nearly all of the oxides which contained no potassium oxide are members of this series.

3. The composition of the compounds precipitated when manganese sulphate is treated with potassium permanganate in the presence of four molecules of nitric acid to one of potassium permanganate is probably $K_2O_{20}MnO_2 + xH_2O$, since in all the analyses in which potassium oxide was determined the ratio of potassium oxide to manganese oxide was nearly 1 : 20.

4. Nearly one-half of the potassium oxide in such compounds is lost by standing under nitric acid.

BIOGRAPHICAL.

The author was born near Woodstock, Ontario, May 4, 1870. His early education was received at the public schools in that vicinity. In 1884 he entered Woodstock College, where he spent four years. In 1888 he entered Toronto University and received the degree of B. A. in 1892. Since that time he has been pursuing his studies in the Johns Hopkins University. He was assistant to Professor Morse for the year '94-'95 and fellow in '95-'96.

